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Henkel KGaA - H 4051
Dr. Endres / KK
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"Process for the treatment of the circulating water in painting booths"

This invention relates to a process for the treatment of the circulating water in painting booths, particularly for vehicle painting. The paint particles washed out of the waste air and introduced into the circulating water are kept in suspension in finely dispersed form and removed from the circulating water continuously or discontinuously. This is achieved by addition of suitable additives to the circulating water, the concentration of which in the circulating water is set to the relatively low values of between 0.01 and 0.5 wt.% based on the circulating water.

In painting booths in which water-based or solvent-based paints are applied to the surfaces to be painted, the entire quantity of paint used is not applied to the intended surface. Rather, a considerable proportion of the paint particles becomes mixed with the air flowing through the painting booth or settles on the walls of the painting booth. The paint particles, the so-called paint overspray, are washed out of the air stream with water by means of suitable washing devices, such as Venturi scrubbers. The water mixed with paint is collected in circulating water tanks and circulated. As the paint particles in the circulating water stick together and to equipment parts, however, they are released and coagulated by traditional methods by the addition of release and coagulation agents. The coagulated paint particles settle or float on the circulating water according to the method employed. The thus-produced paint sludge may be removed from the bottom or the surface of the circulating water tank by means of suitable removal devices. This traditional method requires the use of inorganic or organic release and coagulation agents which may be selected, for example, from sheet silicates, waxes and organic polymers. The quantity used of these products is generally from 10 to 50 wt.% based on the paint overspray ready for spraying. The release of the paint particles and removal of the paint sludge is not, however, usually complete so that paint sludge is deposited and has to be removed by hand from time to time, involving a great deal of work. In addition, an additional quantity of sludge is produced where inorganic coagulants are used, and this leads to additional disposal costs.

There is therefore a need for improved processes for the treatment of the circulating water in painting booths, which may involve a reduced use of chemicals, with which fewer problems caused by sticky paint particles arise and/or in which there is less manual outlay for cleaning and maintaining the painting booths and the disposal costs are distinctly minimized.

In a first embodiment, the present invention provides a process for the treatment of the circulating water in painting booths, wherein the paint particles are dispersed by addition of dispersants which are selected from:

(a) homo- and co-polymers based on maleic acid, acrylic acid and/or methacrylic acid having molecular weights of between 2,500 and 500,000;
(b) non-ionic surfactants;
(c) anionic surfactants, no polyaspartic acid being additionally added to the circulating water in this case;
(d) inorganic or non-polymeric organic complexing agents and mixtures thereof;
the total concentration thereof being between 0.01 and 2.0 wt.%, preferably between 0.02 and 0.5 wt.%, based on the circulating water.

The success of the process according to the present invention is based on the fact that the paint particles remain dispersed in the circulating water and are not deposited as paint sludge which is difficult to remove. The circulating water may therefore be circulated together with the paint particles dispersed therein without equipment parts becoming sticky.

Homo- and co-polymers based on maleic acid, acrylic acid and/or methacrylic acid are intended to mean those polymers wherein at least part of the monomers consists of the above-mentioned polymerizable carboxylic acids. Other polymerizable monomers may be co-incorporated into the polymers. Polymers which exclusively contain acrylic acid and/or methacrylic acid are used, for example. The molecular weight of the polymers is preferably from 15,000 to 250,000, particularly up to 50,000. The polymers may be added to the circulating water as they are or in salt

form. Depending on the pH of the circulating water, the acid/base equilibrium between acid and salt form is automatically adjusted.

In the process according to the present invention, non-ionic surfactants, which are preferably selected from alkoxylates of fatty acids, fatty alcohols or fatty amines having 7 to 36, preferably 10 to 22, carbon atoms in the fatty alkyl group and having 5 to 100, preferably 10 to 80, alkylene oxide units, may be used as dispersants. These alkoxylates may have the terminal groups thereof closed, i.e. represent so-called mixed ethers.

A butyl group may be present, for example, as a terminal group. Ethylene oxide groups or combinations of ethylene oxide groups and propylene oxide groups are considered in particular as alkylene oxide groups. An alkoxylate of a $C_{12/14}$-fatty alcohol mixture with an average of five ethylene oxide and four propylene oxide units in the molecule may be used for example.

Inorganic or non-polymeric organic complexing agents may further be used as dispersants. These are preferably selected from:
(i) organic carboxylic acids having two to ten heteroatoms, which may coordinate on metal ions, particularly from citric acid, tartaric acid, malic acid, gluconic acid, nitrilotriacetic acid, ethylenediamine tetraacetic acid, methylglycine diacetic acid;
(ii) organic phosphonic acids, particularly from 1-hydroxyethane-1,1-diphosphonic acid, aminotrimethylene phosphonic acid and phosphonobutane tricarboxylic acid;
(iii) oligomeric or polymeric inorganic phosphates, particularly Na triphosphate, Na pyrophosphate and Na hexametaphosphate.

Oxygen atoms (alcohols, carboxylates) or nitrogen atoms are considered in particular as heteroatoms of the organic complexing agents which may coordinate on metal ions.

It is also applicable in each case that the complexing agents may be used in the form of the acids or in salt form. Depending on the pH of the circulating water, a mixture comprising acid and salt form will be reached according to the acid/base equilibrium.

The organic complexing agents should not be polymers and should differ in this way from the polymeric carboxylic acids of (a), which also have complexing properties. The inorganic complexing agents may, however, be entirely polymeric, such as Na pyrophosphate.

Mixtures of representatives of the individual groups of dispersants listed may also be used. Mixtures comprising polyacrylates and phosphonic acids and mixtures comprising niosurfactants and phosphonic acids are particularly suitable.

Where dispersants selected from (a), (b) and (d) are used, 0.2 to 2 wt.%, based on the circulating water, of polyaspartic acid may be additionally added to the circulating water. The use of polyaspartic acid as such is known from patent application PCT/EP99/00350, which is not a prior publication. According to this document, the polyaspartic acid may be used together with anionic surfactants. In the process according to the present invention, however, anionic surfactants may also be used without the co-use of polyaspartic acid. The anionic surfactants to be used as dispersants are preferably selected from soaps, alkyl sulfates, alkyl sulfonates, alkylbenzene sulfonates, alkylether sulfates each having 7 to 44, preferably 8 to 22, carbon atoms in the alkyl group, and from sulfonated maleic acid esters.

In the process according to the present invention, the pH of the circulating water is preferably adjusted to a range between about 5 and about 10.5. A weakly alkaline pH may be preferred. Particularly where phosphonic acids are used as dispersants, particularly advantageous results are obtained when the pH in the circulating water is between about 8 and about 10. At such a pH, dispersants capable of protolysis will be mainly present in salt form, irrespective of the form in which they are introduced into the circulating water. Depending on the form in which the dispersants are used, it may be necessary additionally to use pH adjusters, such as alkali metal hydroxides, to give the preferred pH range.

Depending on the type of paint used, it may further be advisable additionally to add defoaming agents to the circulating water. The use of defoaming agents is generally

known in the technical field in question as foam problems may arise in the circulating water particularly where water-based paints are used.

The process according to the present invention is particularly suitable for painting equipment in which the circulating water exhibits high turbulence. The dispersing effect of the dispersants to be used according to the present invention is increased by the flowing of the circulating water.

When the dispersants according to the present invention are used, the circulating water may be circulated for a certain period of time without the need to remove the entrained paint particles. If the equipment is operated for a fairly long time, however, as time progresses a concentration of paint particles in the circulating water is reached which should not be further exceeded in order to prevent breakdowns. The range in which this concentration limit lies depends on the actual design of the equipment in question. For this reason, the process according to the present invention preferably provides for the removal of a proportion of the paint particles from the circulating water continuously or discontinuously. The preferred procedure in this case is to separate some of the paint particles from the circulating water by means of a membrane filtration, preferably an ultra filtration. The permeate of the membrane filtration is returned to the circulating water and the retentate disposed of. For this purpose, a portion of the circulating water may be passed over the membrane via a by-pass discontinuously or continuously.

The process according to the present invention functions particularly reliably when it may be ensured, by addition of the dispersants to the circulating water in a concentration between 0.01 and 2.0 wt.% based on the circulating water, that the paint particles in the circulating water have an average particle size, which may be determined by means of laser diffraction, of below about 20 μm. To achieve this, an addition of suitable dispersants is required for circulating water of a hardness of at least 2 °dH (German hardness) (corresponds to 0.714 mval/l of alkaline earth metal ions).

Accordingly, in a generalized aspect, the present invention relates to a process for the treatment of the circulating water in painting booths wherein the circulating water has a hardness of at least 2° German hardness and wherein the paint particles are dispersed by addition of dispersants in a concentration between 0.01 and 2.0 wt.% based on the circulating water in such a way that they exhibit an average particle size, which may be determined by means of laser diffraction, of below 20 μm.

Laser diffraction is an example of a method of measurement of particle sizes in the micrometer range, in which the light scatter brought about by the particles is measured. A particle size measuring instrument made by Sympatec may be used for this purpose, for example. The average particle size is defined as that particle size which establishes when the particles are kept in suspension by a slight movement of the suspension, for example, by stirring. Ultrasound, which mechanically destroys the particles, is not used in this case.

The above statements apply to the dispersants which may be used under this generalized aspect of the present invention. This also applies to the preferred procedure described above.

In the two embodiments expressed by the independent claims, the present invention is suitable for dispersing water-based and/or solvent-based paints.

Examples

Herberts' water-based metallic paint Aqua Pearl Base, Siena red II was used for the trials. In each case, a quantity of test paint was introduced into water so that the paint solids content was 0.5 wt.% based on the amount of water. Düsseldorf/Benrath tap water, which has a hardness of 18 °dH (corresponding to 6.426 mval/l of alkaline earth metal ions) was used as the water.

In a first set of trials, Sympatec's particle size measuring instrument based on laser diffraction was used to measure the average particle size (defined as 50% value) which was established under gentle stirring using the various dispersants. The results are contained in Table 1.

Table 1: Average particle size (50% value)

Example	Dispersant/quantity with respect to water	50% value (μm)
Ref. 1	none	255
Example 1	Coconut amine x 12 EO[(1)], 0.25%	11.8
Example 2	Coconut amine x 12 EO[(1)], 0.25% + polyaspartic acid, 0.76%	11.3

[(1)] EO = ethylene oxide

In the above set of trials, it was shown that the particle size correlates to the stability of the paint suspension: at a particle size below about 20 μm, no sedimentation or flotation may be observed, even 30 minutes after the dispersion was prepared. Paint does not settle on the glass wall of the test vessel. Further dispersants were therefore only then tested to see whether they exhibit this behavior. Table 2 contains examples.

Table 2: Dispersibility: dispersion stability after 30 minutes

Ex. No.	Dispersant quantity (wt.% based on water)	Dispersion stable?	Paint on vessel wall?
Ref. 2	none	no (flotation)	yes
Ref. 3	polyaspartic acid, 0.76%	no (flotation)	no
Ex. 3	modified polyacrylic acid molecular weight 4000, 0.23%	yes	no
Ex. 4	coconut amine x 12 EO	yes	no
Ex. 5	sulfosuccinic acid-bis-2-ethylhexylester, Na salt, 0.38%	yes	no
Ex. 6	Na oleate, 0.5%	yes	no

The sediment volume was quantitatively determined in a further set of trials. For this purpose, the dispersant was placed in a liter of water and stirred for 10 minutes at 300 rpm. The test paint described above was then added in a quantity such that the paint solids content was 0.5 wt.% based on the water. Stirring was repeated for 10 minutes at 300 rpm. The dispersion was then transferred into a measuring funnel (Imhoff cone) and the sediment volume, in ml, measured after a residence time of 10 minutes. Good dispersion is evident from the fact that no sediment appears. Table 3 contains the results.

Table 3: Sediment volume

Ex. No.	Dispersant quantity (wt.% based on water)	Sediment volume (ml)
Ref. 4	none	100
Ref. 5	polyaspartic acid, 0.2%	2.5
Ex. 7	polyacrylate (molecular weight 10,000), 0.18%	0
Ex. 8	maleic acid/olefin copolymer (molecular weight 12,000), 0.13%	0
Ex. 9	polyacrylate (molecular weight 30,000), 0.2%	0
Ex. 10	maleic acid/acrylic acid copolymer (molecular weight 70,000), 0.2%	0
Ex. 11	coconut amine x 12 EO, 0.1%	0
Ex. 12	Na tripolyphosphate, 0.5%	0
Ex. 13	Na pyrophosphate, 0.5%	0
Ex. 14	Na hexametaphosphate, 0.5%	0
Ex. 15	citric acid, 0.5%	0
Ex. 16	1-hydroxyethane-1,1-diphosphonic acid, 0.3%	0
Ex. 17	aminotrimethylene phosphonic acid, 0.25%	0
Ex. 18	phosphonobutane tricarboxylic acid, 0.25%	0
Ex. 19	nitrilotriacetic acid, 0.2%	0
Ex. 20	$C_{16/18}$-fatty alcohol x 25 EO, 0.5%	0
Ex. 21	$C_{16/18}$-fatty alcohol x 80 EO, 0.5%	0
Ex. 22	coconut amine x 15 EO, 0.5%	0
Ex. 23	$C_{12/14}$-fatty alcohol sulfate, 0.18%	0
Ex. 24	ring-opened soya polyol x 10 EO, 0.5%	0